

# Influence of nickel on the electrochemical activity of PtRu/multiwalled carbon nanotubes electrocatalysts for direct methanol fuel cells

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**Abstract** This paper presents the effect of Ni in PtRu electrocatalysts over multiwalled carbon nanotubes (MWCNT) utilized for the electro-oxidation of methanol with the purpose of increasing reaction activity and tolerance to carbon monoxide. Two kinds of MWCNT were prepared using the same technique but different catalytic agents, ferrocene, and nickelocene. MWCNT obtained from ferrocene were treated after the synthesis to eliminate amorphous carbon and Fe excess, while MWCNT from nickelocene were used as synthesized to leave the nickel nanoparticles formed during the synthesis. PtRu particles were deposited over the surface of both types of MWCNT in order to study the effect of the Ni presence. The structure of the electrocatalysts was analyzed by transmission electron microscopy (TEM) and X-ray diffraction (XRD). Chemical elemental microanalysis was carried out by X-ray energy dispersive spectroscopy (EDS). The synthesized MWCNT had an average diameter in the order of 60 nm and an average length of about 30 microns. Metallic

nanoparticles deposited had a particle size in the order of 10 nm each. The electrochemical surface area (ESA) was measured using CO stripping curves and the activity toward the methanol oxidation reaction was evaluated. The ESA was improved with the presence of Ni, achieving an activity and onset potential similar to a commercial electrocatalyst (20 wt% PtRu/C, ETEK) with a lower PtRu loading (10 wt% PtRu).

**Keywords** Carbon nanotubes · PtRuNi nanoparticles · Methanol fuel cells · Methanol electro-oxidation

## 1 Introduction

Direct methanol fuel cell (DMFC) is a technology in the process of development. It is of great interest due to the wide range of mobile applications. The use of DMFCs could potentially solve different problems in the fuel cell area, such as hydrogen storage and transportation.

In DMFCs, the oxidation of methanol takes place at the anode of the cell according to



takes place at the anode of the cell. Pt electrodes are active for the oxidation of methanol; however, CO groups strongly adsorb on the Pt sites causing the poisoning of the catalyst [1], hence it is necessary for the addition of a second metal. Typically, Pt Ru catalysts are used in DMFCs, demonstrating by far to be the best ones for reaction (Eq. 1). Lima et al. [2] established that Ru provides oxygenated species creating additional active sites for the adsorbed CO oxidation. However, efforts are required in this area in order to decrease the metal loading and in consequence the production costs of the DMFCs.

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The idea to include a third metal in the catalyst or moreover to replace Ru with a different metal is getting more and more interest by different research groups. Non-noble metals do not have high activity for the oxidation of methanol; however, there may exist a synergetic effect produced by the interaction between two and three metals that could cause an improvement on the oxidation rate at lower noble metal loadings. The inclusion of nickel (a low cost metal) particles in catalysts has been studied by different authors [2–5] who have reported that the activity and CO tolerance of the electrocatalysts can be improved.

On the other hand, it has been demonstrated by different researchers that multiwalled carbon nanotubes (MWCNT) are a good support for metal particles [6–8]. Due to their characteristics, the MWCNT provide stability and good electronic conductivity to the catalytic system. Furthermore, metal particles can be well dispersed in the MWCNT surface; this distribution allows the particles to be easily exposed and available for the electrochemical reaction.

Within this context, the objective of this work is to evaluate the performance of MWCNT with Ni particles as support of PtRu nanoparticles for the oxidation of methanol. The Ni particles were incorporated during the synthesis of the MWCNT. This provides an advantage on the support, as it simplifies the cleaning process of the nanotubes after their synthesis, and can potentially provide a synergistic effect on the oxidation reaction rate of methanol.

## 2 Experimental methods

### 2.1 Electrocatalysts synthesis

Two types of MWCNT were used as support for the electrocatalysts. The first type was synthesized following the methodology previously reported by Valenzuela et al. [9], using ferrocene (Fluka, 98 %) as catalytic agent. For the second type of MWCNT, the catalytic agent was nickelocene (Sigma Aldrich, 98 %). The intention of using nickelocene as a catalytic agent was to evaluate the potential advantage of the metallic Ni particles formed during the synthesis on the oxidation of methanol. In both cases, toluene (J.T. Baker, 98 %) was used as the carbon source and a Vycor tubing (diameter of 9 mm) was used as the substrate. In the case of the MWCNT where nickelocene was used, a metallic oxide (MnO) was previously deposited inside the Vycor tubing in order to promote a better growth of the MWCNT. Only the MWCNT obtained from ferrocene were cleaned in a reflux system ( $\text{HNO}_3$ , 12 h, 120 °C) to remove remains of iron from the surface.

Pt and Ru particles were deposited over the MWCNT (both types) using ammonium hexachloroplatinate

$(\text{NH}_4)_2\text{PtCl}_6$ , Alfa Aesar 43.78 %), and ruthenium chloride ( $(\text{RuCl}_3)$ , Alfa Aesar 38.51 %), respectively, with an ultrasound assisted aqueous deposition method. In order to get the particles in a metallic form, the materials were treated following a thermal reduction method reported before [10]. The samples were placed inside a tubular furnace at 400 °C and reduced with a 10 %  $\text{H}_2$  in  $\text{N}_2$  atmosphere during 4 h. The intent was to achieve loadings of 10 wt% Pt and 10 wt% Ru, for both types of MWCNT (synthesized with ferrocene and nickelocene).

### 2.2 Characterization and electrochemical evaluation

The chemical composition of the synthesized materials was performed by energy dispersive X-ray spectroscopy (EDS) in a JEOL JSM-6390 scanning electron microscope; the crystalline structure and phases of the materials were analyzed by X-ray diffraction (XRD) in a Phillips X Pert MPD diffractometer ( $\lambda = 1.54056 \text{ \AA}$  at 43 kV and 30 mA); and the particle size of the materials and distribution was determined by transmission electron microscopy (TEM) in a JEOL JEM-2200FS.

Electrochemical measurements were carried out using a three-electrode cell with 0.5 M  $\text{H}_2\text{SO}_4$  (Fisher Scientific, 98 %) as electrolyte. Pt foil with an area of  $2 \text{ cm}^2$  was used as counter electrode, Ag/AgCl (Sat KCl), and glassy carbon ( $0.9163 \text{ cm}^2$ ) as reference and working electrodes, respectively. All the measurements were performed in a Solartron SI 1287 potentiostat/galvanostat. The preparation of the ink used in the working electrodes as well as the procedure to deposit it on the working electrodes has been described in detail in the literature by Valenzuela et al. [11].

The electrochemical cell was purged with argon (Praxair 99.999 %) to remove oxygen gas present in the electrolyte solution. The surface of the electrode was cleaned through an electrochemical process (20 cycles from  $-0.25$  to  $1 \text{ V}$  versus Ag/AgCl reference electrode at  $100 \text{ mV s}^{-1}$ ) prior to each experiment to avoid surface blockage due to the presence of intermediates. For the CO stripping test, CO (Praxair 99.99 %) was bubbled into the cell for 7 min, while holding the potential at  $-0.2 \text{ V}$  to achieve adsorption of CO on the surface of the metallic active particles. The cell was then purged with argon gas (for a period of 10 min) to remove traces of CO from the electrolyte. Then, cyclic voltammetry tests were carried out from  $-0.20$  to  $1.2 \text{ V}$  versus Ag/AgCl reference electrode at  $10 \text{ mV s}^{-1}$  for two cycles. The electrochemical surface area (ESA) was calculated using the cyclic voltammetry curves of the first cycle, integrating the CO oxidation region of the curve and using the equation and methodology reported by Pozio et al. [12].

To characterize the electrocatalyst toward the methanol oxidation reaction, 0.5 M methanol was added to the

supporting electrolyte (0.5 M H<sub>2</sub>SO<sub>4</sub>). The measurements were performed using the same conditions described above for the cyclic voltammetry tests. The performance of the electrodes was compared with a commercial material, 20 % PtRu/Vulcan from Etek. The electrodes prepared with the commercial material were made using the same methodology as that described for the MWCNT-supported materials (an ink was prepared and deposited on the substrate [11]).

### 3 Results and discussion

#### 3.1 Microstructural characterization

Elemental analysis by EDS in a scanning electron microscope (SEM) was performed to determine the composition and the loading of the catalysts; the results are presented in Table 1. The concentration of Pt is higher than Ru for both of the electrodes materials about 9 and 3 wt% of Pt and Ru, respectively. The electrocatalyst without Ni exhibits a total metal loading on the MWCNT of about 12 wt% (assuming that the Fe is inside the nanotubes and not on the surface). The electrocatalyst with Ni shows a total loading of 10 wt% of Pt–Ru, and about 9 wt% of Ni. Due to the growth mechanism associated with the spray pyrolysis technique, Ni particles remain not only inside the nanotube but also on the MWCNT surface and are expected to contribute to the electrochemical activity.

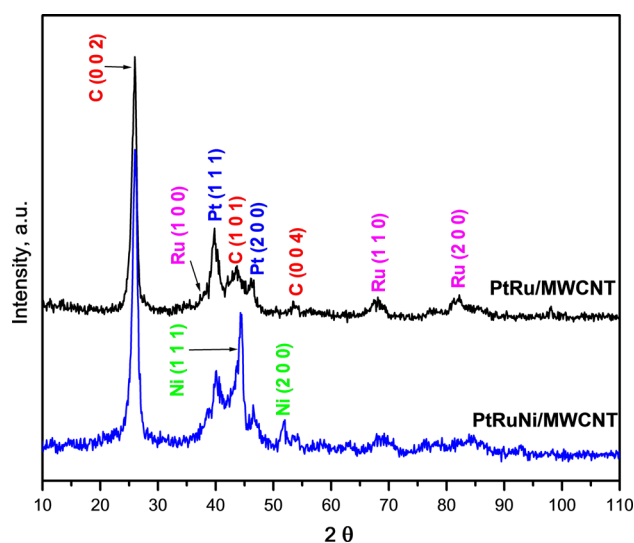
It is known that Pt–Ru bimetallic electrocatalysts provide good performance and tolerance to CO poisoning in DMFCs. The metallic particles need to be close enough to generate an interaction. Some authors [8, 13] propose that the alloy degree has a direct influence to the activity; however, Liang et al. [5] proposed that a good contact between metallic particles is enough to improve the electrocatalytic activity. XRD diffraction experiments were performed to have information about the phases and crystallinity of the synthesized materials. Figure 1 shows the diffraction patterns of the samples, characteristic intensities for the structure of the MWCNT, as well as for the metallic particles of Pt, Ru, and Ni are observed. According to these results it could be suggested that particles are not alloyed.

**Table 1** Elemental analysis obtained by EDS–SEM

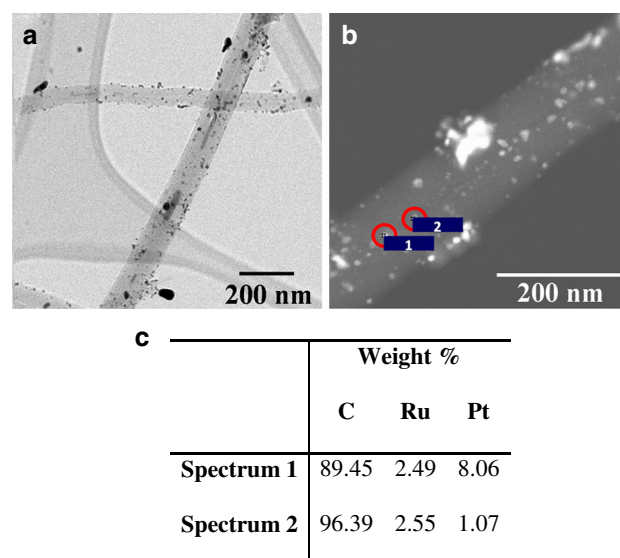
Catalyst	wt%					
	C	O	Pt	Ru	Fe	Ni
PtRu/MWCNT	84.4	2.3	8.8	3.1	1.3	–
PtRuNi/MWCNT	79.6	1.1	7.1	2.9	–	9.2

Figure 2a presents a TEM micrograph of the sample PtRu/MWCNT, the catalyst particles are dispersed over the MWCNT walls and have average particle size between 5 and 10 nm. On the other hand, Fig. 2b shows an image with two points where a punctual microanalysis was performed. Pt and Ru particles were identified close to each other in a punctual analysis summarized in Fig. 2c.

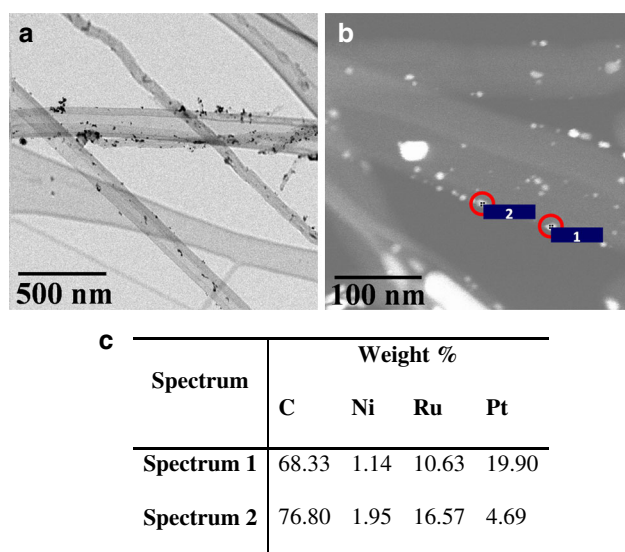
TEM images of the PtRuNi/MWCNT samples are shown in Fig. 3a. The average size of the particles is between 5 and 8 nm. Agglomerates are also observed that could be attributed to the amorphous carbon and residues of Ni clusters from the MWCNT synthesis procedure. The



**Fig. 1** X-ray diffractograms of the MWCNT



**Fig. 2** TEM images of the PtRu/MWCNT. **a** Bright field, **b** areas of the punctual elemental analysis and **c** elemental analysis results

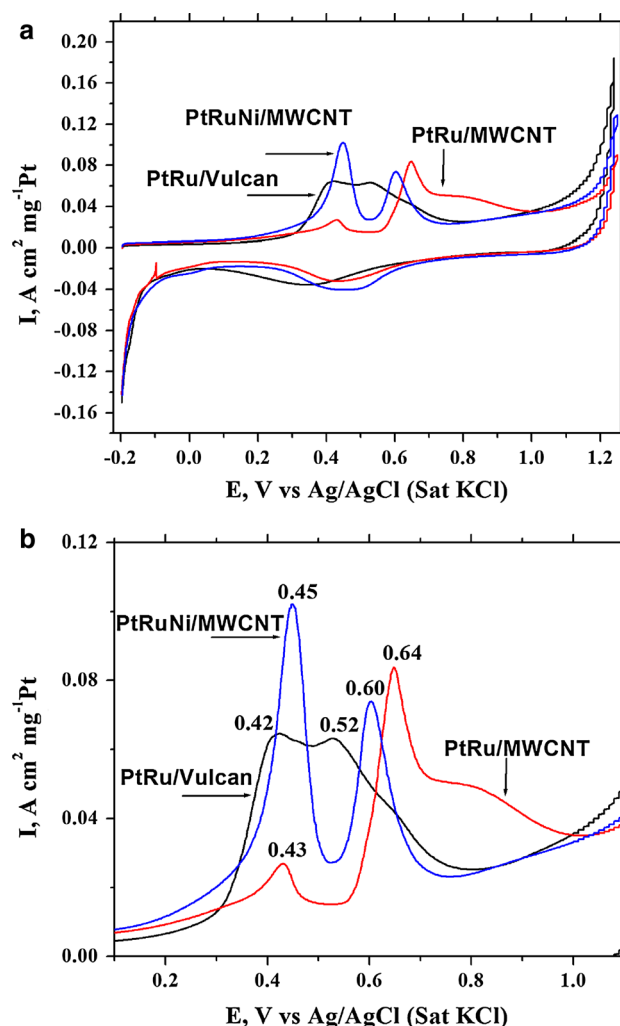


**Fig. 3** TEM of the PtRuNi/MWCNT. **a** Bright field, **b** areas of the punctual elemental analysis and **c** elemental analysis results

microanalysis is presented on the points in Fig. 3b and the results of the EDS analysis are shown in Fig. 3c. The punctual analysis reveals that there is a presence of metallic Ni particles on the surface and close to the Pt and Ru particles. It is hypothesized that this proximity among Ni, Pt, and Ru particles could cause a synergistic effect in the electrochemical activity.

### 3.2 Electrochemical activity

CO stripping has been used by different authors [14, 15] to obtain the electrochemical active area of PtRu electrocatalysts, as well as to determine the tolerance of the catalysts to CO poisoning. Figure 4 presents the cyclic voltammetry curves obtained during the CO stripping tests of the electrodes prepared with the synthesized MWCNT samples and with the reference commercial sample (PtRu/Vulcan Etek). Only the first cycle of the voltammetry, where the absorbed CO was completely oxidized, is presented. The samples exhibit oxidation peaks in the region of PtRu materials, with onset potentials very close to the PtRu/Vulcan reference (Fig. 4a). Opposite case is the shape of the curves; both PtRu/MWCNT and PtRuNi/MWCNT electrocatalysts show two well-defined peaks unlike the commercial material that exhibits two overlapped peaks. This behavior could be related to the characteristics of the supporting material rather than the metallic catalyst particles as it was established by Jiwei Ma et al. [16]. In Ma's research work, it is explained that the occurrence of two defined peaks is related to different electron densities of Pt, being this directly influenced by the graphitic domains of carbon



**Fig. 4** CO stripping voltammograms of the samples and the commercial material: **a** complete potential window and **b** close up of the CO oxidation region in the forward scan. Measurement conditions were  $10 \text{ mV s}^{-1}$ , in a potential range of  $-0.2$  to  $1.2 \text{ V}$  versus Ag/AgCl (Sat KCl)

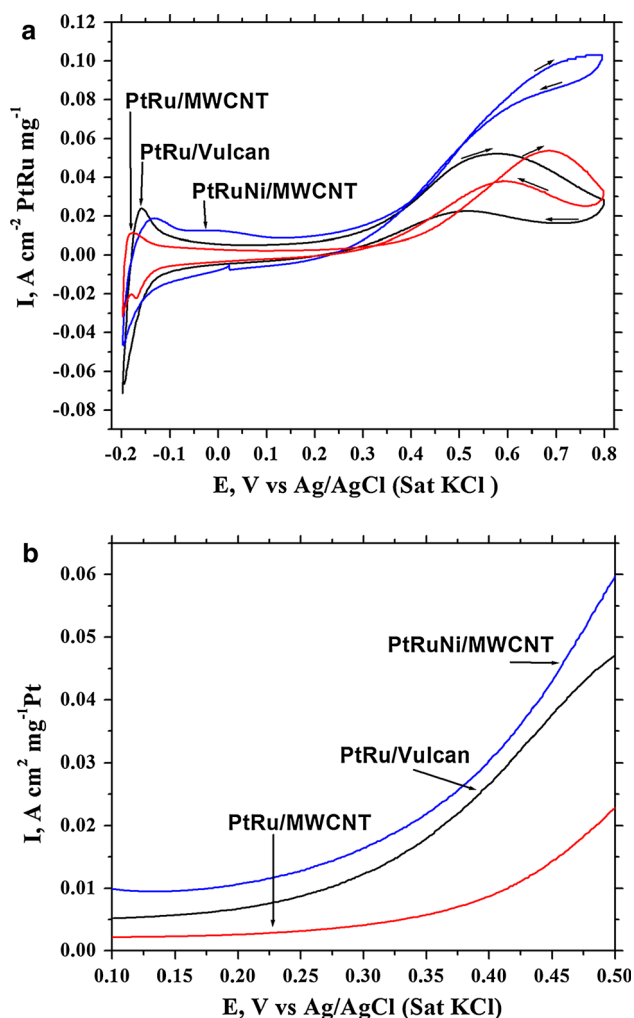
(support). For Pt-MWCNT, this electron density is higher than for Pt-Vulcan.

It is well known that the inclusion of a second metal decreases the onset potential for CO oxidation compared to the materials with pure Pt, this is attributed to a bifunctional reaction mechanism [17] that makes these materials tolerant to CO poisoning (and makes them a good option for the oxidation of methanol). According to the ESA shown in Table 2, the synthesized materials achieved activities comparable to the PtRu/Vulcan. This is an excellent performance taking into consideration that the metal loading is nearly half less of the reference material. It is important to observe that the presence of Ni increased the ESA compared to the sample without Ni. Leaving the Ni particles (residues of the MWCNT synthesis reaction) on the MWCNT represents some advantages, since the



**Table 2** Electrochemical characteristics of the materials

Catalyst	ESA (m <sup>2</sup> g <sup>-1</sup> )	On set potential <sup>a</sup> (V)	Pt–Ru (wt%)
PtRu/Vulcan	306	0.3	20
PtRu/MWCNT	273	0.4	12
PtRuNi/MWCNT	306	0.3	10

<sup>a</sup> Obtained by cyclic voltammetry in the presence of methanol**Fig. 5** Cyclic voltammograms in the presence of methanol performed to the samples and the commercial material. Measurement conditions were 10 mV s<sup>-1</sup>, in a potential range of -0.2 to 0.8 V versus Ag/AgCl (Sat KCl). The inset is a close up of the curves in the onset potential region

surface cleaning process is not necessary, the electrocatalysts production costs could be decreased, while keeping or even increasing the ESA. Liang et al. [5] suggested that the inclusion of Ni in a PtRu system can create new active sites at the interface. The study established that the improvement in the activity toward the CO oxidation that is related

to the formation of nickel hydroxide in acid medium, which provides a high electron and proton conductivity, consequently PtRuNi/MWCNT present higher ESA than PtRu/MWCNT.

The electrochemical performance of the electrodes was evaluated for the oxidation of methanol using cyclic voltammetry. The results are shown in Fig. 5. The PtRuNi/MWCNT electrocatalyst exhibited the highest current density, followed by the PtRu/MWCNT electrode and the PtRu/Vulcan electrode. The inset in the figure shows a close up of the onset potential region where it is easy to appreciate that the PtRuNi/MWCNT start the reaction at the same potential that of the commercial material, the values are summarized in Table 2.

## 4 Conclusions

The utilization of MWCNT synthesized from a catalytic agent containing Ni, as support for Pt and Ru particles was demonstrated and provides various advantages: (1) the MWCNT cleaning process after the synthesis is avoided reducing the number of steps on the production of the electrocatalysts production, which could lead to a decrease in the manufacturing costs of the electrocatalyst; (2) the presence of the Ni particles provides improvements in the electrochemical characteristics of the material, such as achieving high ESA, being CO tolerant, and having a good activity for the methanol oxidation reaction. Moreover, it is possible to accomplish the above-mentioned advantages with a lower loading of PtRu. The synergy produced from the interaction of the three metals causes an increase in the activity, positioning these types of materials as an option to reduce the Pt loading without sacrificing activity. Hence, the obtained electrocatalysts could be used for the electro-oxidation of other alcohols or organic molecules. In order to establish a suitable mechanism reaction it is necessary to carry out more studies, particularly about the interaction of the particles with the support. Also, extensive investigation on their stability is recommended.

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## References

1. Jung-Ho W, Kwan-Young L (2006) Overview of the development of CO-tolerant anode electrocatalysts for proton-exchange membrane fuel cells. *J Power Sources* 157:128–135

2. Lima A, Coutanceau C, Leger JM, Lamy C (2001) Investigation of ternary catalysts for methanol electrooxidation. *J Appl Electrochem* 31:379–386
3. Park K-W, Choi J-H, Kwon B-K, Lee S-A, Sung Y-E, Ha H-Y, Hong S-A, Kim H, Wieckowski A (2002) Chemical and electronic effects of Ni in Pt/Ni and Pt/Ru/Ni alloy nanoparticles in methanol electrooxidation. *J Phys Chem B* 106:1869–1877
4. Martínez-Huerta MV, Rojas S, Gómez de la Fuente JL, Terreros P, Peña MA, Fierro JLG (2006) Effect of Ni addition over PtRu/C based electrocatalysts for fuel cell applications. *Appl Catal B* 69:75–84
5. Liang Y, Zhang H, Tian Z, Zhu X, Wang X, Yi B (2006) Synthesis and structure-activity relationship exploration of carbon-supported PtRuNi nanocomposite as a CO-tolerant electrocatalyst for proton exchange membrane fuel cells. *J Phys Chem B* 110:7828–7834
6. Ocampo AL, Miranda-Hernandez M, Morgado J, Montoya JA, Sebastian PJ (2006) Characterization and evaluation of Pt–Ru catalyst supported on multi-walled carbon nanotubes by electrochemical impedance. *J Power Sources* 160:915–924
7. Jiang Z, Jiang Z-J (2011) Improvements of electrocatalytic activity of PtRu nanoparticles on multi-walled carbon nanotubes by a H<sub>2</sub> plasma treatment in methanol and formic acid oxidation. *Electrochim Acta* 56:8662–8673
8. Huang T, Liu J, Li R, Cai W, Yu A (2009) A novel route for preparation of PtRuMe (Me = Fe, Co, Ni) and their catalytic performance for methanol electrooxidation. *Electrochem Commun* 11:643–646
9. Valenzuela-Muñoz AM, Verde Y, Miki-Yoshida M, Alonso-Núñez G (2008) Synthesis of multi-walled carbon nanotubes by spray-pyrolysis using a new iron organometallic complex as catalytic agent. *J Nanosci Nanotechnol* 8:6456–6460
10. Verde Y, Alonso-Núñez G, Miki-Yoshida M, Jose-Yacaman M, Ramos VH, Keer A (2005) Active area and particle size of Pt particles synthesized from (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub> on a carbon support. *Catal Today* 107–108:826–830
11. Valenzuela-Muñoz AM, Alonso-Núñez G, Miki-Yoshida M, Botte GG, Verde-Gómez Y (2013) High electroactivity performance in Pt/MWCNT and PtNi/MWCNT electrocatalysts. *Int J Hydrogen Energy* 38–28:12640–12647
12. Pozio A, De Francesco M, Cemmi A, Cardellini F, Giorgi L (2002) Comparison of high surface Pt/C catalysts by cyclic voltammetry. *J Power Sources* 105:13–19
13. Prabhuram J, Zhao TS, Liang ZX, Chen R (2007) A simple method for the synthesis of PtRu nanoparticles on the multi-walled carbon nanotube for the anode of a DMFC. *Electrochim Acta* 52:2649–2656
14. Hsu N-Y, Chien C-C, Jeng K-T (2008) Characterization and enhancement of carbon nanotube-supported PtRu electrocatalyst for direct methanol fuel cell applications. *Appl Catal B* 84: 196–203
15. Wang W, Wang R, Wang H, Ji S, Key J, Li X, Lei Z (2001) An advantageous method for methanol oxidation: design and fabrication of a nanoporous PtRuNi trimetallic electrocatalyst. *J Power Sources* 196:9346–9351
16. Ma J, Habrioux A, Morais C, Lewera A, Vogel W, Verde-Gómez Y, Ramos-Sanchez G, Balbuena P, Alonso-Vante N (2013) Spectroelectrochemical probing of the strong interaction between platinum nanoparticles and graphitic domains of carbon. *ACS Catalysis* 3(9):1940–1950
17. Hamnett A (1997) Mechanism and electrocatalysis in the direct methanol fuel cell. *Catal Today* 38:445–457